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Far-Field Super-Resolution Mapping of Localised Surface Plasmons and Nano-Antennas

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14. ABSTRACT

In the first six months a nanoantennas with resonances at a position suitable for this project was fabricated. A dye emitting in a region matched to this was identified (ATTO 647N) and deposited on the antennas. Confocal fluorescence measurements on this sample showed that the dye emitted more light in the vicinity of the antennas, hinting that the nanoantennas enhanced the fluorescence of the dye.
At the 12 month mark the following achievements were reported: 1) the polymer films used as matrix to host the dyes were greatly improved, leading to smoother surfaces. The concentration of dye in the film was optimized to provide maximum fluorescence without self-quenching; 2) implemented the tools required to conduct lifetime measurements *in house*, along with Fluorescence Lifetime Imaging Microscopy. Lifetime measurements are now routine in the lab; 3) more antennas were produced, but unfortunately no fluorescence enhancement were observed. Further characterization of the antennas by SEM has shown that they were not fit for purpose because of faulty shapes; 4) work began on developing the theory and simulation background to be able to understand in depth the processes at play when the STED technique is used with highly scattering objects (metal particles/antennas), with Dr. Yonatan Sivan (Newton Fellow in the group of Prof. Sir John Pendy) ; 5) the influence of antennas on lifetime as been studied theoretically, with Dr. Vincenzo Giannini, and the outcomes have been published in *Small.*
In the last 6 months of this effort a new dye was identified which was more prone to have its fluorescence properties enhanced by nanoantennas. New sets of antennas were produced, with reproducible properties, and gap small enough to lead to large field enhancements. Combining those two ingredients, it demonstrates that you can observe fluorescence enhancement fostered by plasmonic antennas.
Concurrently, a full modelling of the STED process in the vicinity of nanoantennas has been developed, which we believe will point towards a new way of biological imaging.

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Far-field super-resolution mapping of localised surface plasmons and nano-antennas

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18 – month report

Summary of 6-month report:

In the first document, we reported that we have been able to fabricate nanoantennas with resonances at a position suitable for this project. A dye emitting in a region matched to this has been identified (ATTO 647N) and deposited on the antennas. Confocal fluorescence measurements on this sample have shown that the dye emitted more light in the vicinity of the antennas, hinting that the nanoantennas enhanced the fluorescence of the dye. Figure 1 presents an example of such results.

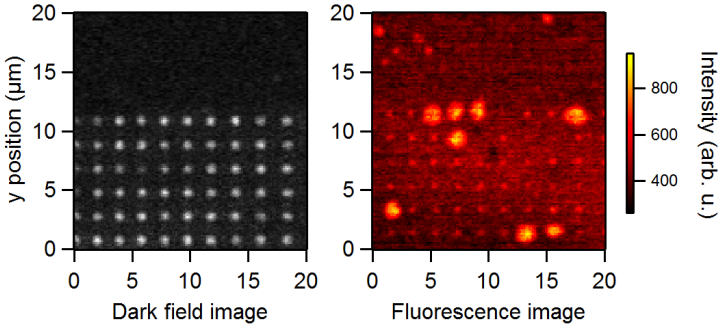

Figure 1: Nano-antenna enhanced fluorescence. Left: dark field scattering image (grayscale) of nanoantennas coated with a fluorescent ATTO film. Right: fluorescence map of the same region, showing an increase of signal on the antennas location.

Summary of 12-month report:

Further the developments reported after 6 months, at the 12 month mark we reported the following achievements:

- The polymer films used as matrix to host the dyes have been greatly improved, leading to smoother surfaces. The concentration of dye in the film has been optimized to provide maximum fluorescence without self-quenching.
- We implemented the tools required to conduct lifetime measurements *in house*, along with Fluorescence Lifetime Imaging Microscopy. Lifetime measurements are now routine in our lab.
- More antennas were produced, but unfortunately no fluorescence enhancement has been observed. Further characterization of the antennas by SEM has shown that they were not fit for purpose because of faulty shapes.
- Work has begun on developing the theory and simulation background to be able to understand in depth the processes at play when the STED technique is used with highly scattering objects (metal particles/antennas), with Dr. Yonatan Sivan (Newton Fellow in the group of Prof. Sir John Pendy).

- The influence of antennas on lifetime as been studied theoretically, with Dr. Vincenzo Giannini, and the outcomes have been published in *Small.*

Methods and Procedures:

Further to these developments, we have optimized the antenna nanofabrication process and are now able to routinely produce antennas with very well-defined shapes.
We have also investigated the possibility to use different dyes, with lower quantum yields, for which fluorescence enhancement due to coupling to nano-antennas should be more pronounced. The theoretical and numerical side of our project – describing the STED process in the vicinity of highly scattering objects such as nano-antennas, has further well advanced, and we will provide a full assessment in our final report.

Results and discussion:

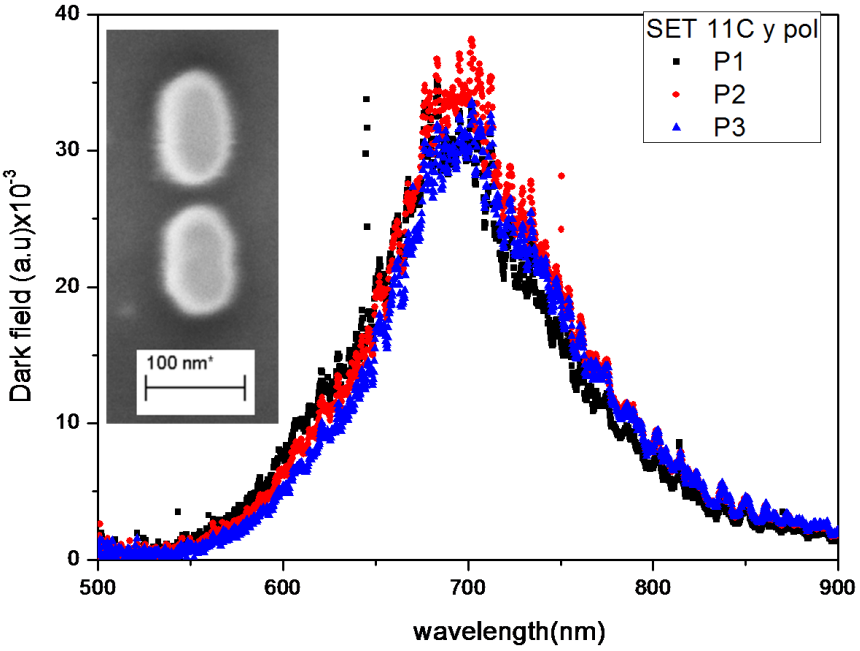

Figure 2: Scattering cross section of typical antennas, measured by dark field spectroscopy. Inset: typical SEM image of a single plasmonic antenna.

- **New batches of antennas**

New antennas have been fabricated in collaboration with the group of Prof. Hong Minghui, at the National University of Singapore. Gold antennas have been obtained by e-beam lithography on glass coverslips. The process here uses ion milling to obtain the antennas, rather than lift-off. This allowed for the production of antennas with better profiles, smaller gaps, and more reproducibly. Figure 2 presents dark field spectra acquired from typical antennas of the samples, as measured in our laboratory. The inset shows an SEM micrograph of a typical antenna of the sample.

- **New fluorophore with low quantum yield**

We have identified Tetraphenylporphyrin (TPP) as an alternative dye more suitable for enhancement studies in the vicinity of nanoantennas. It is a dye with a quantum yield of 11%, absorbs in the blue and emits in the red. We have optimized the deposition of thin films of PMMA doped with TPP, ensuring that the films are smooth and that the

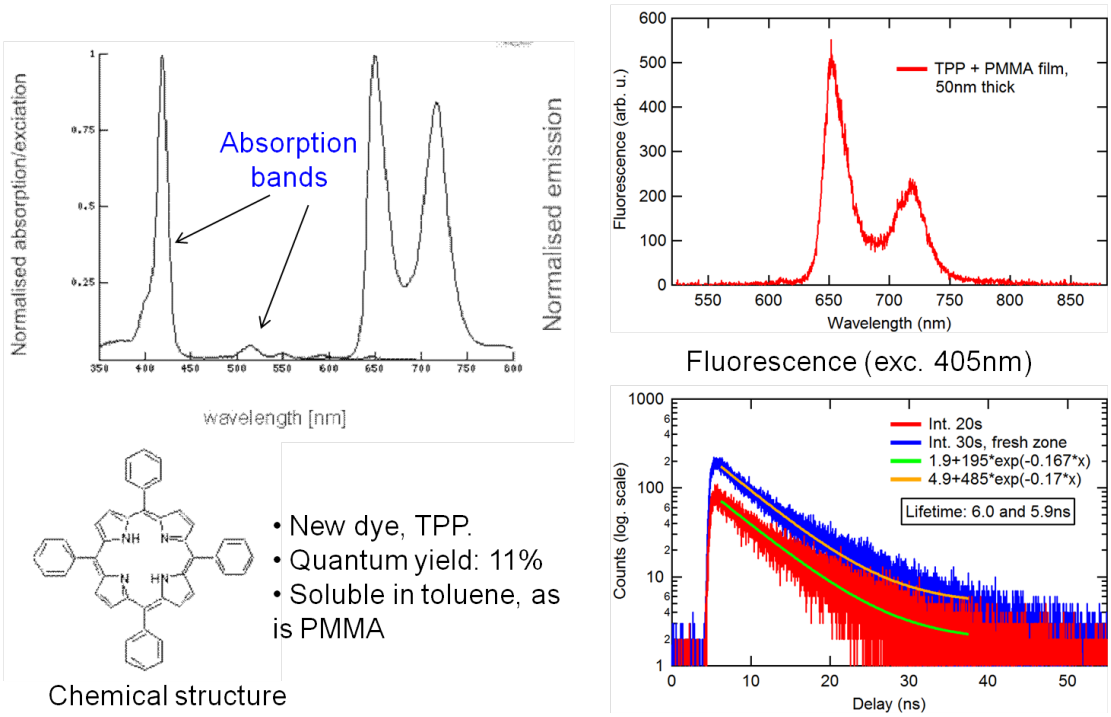

Figure 3: Characterisation of the luminescence of TPP. Top left: absorption and emission cross sections, from literature. Bottom left: Chemical structure of the dye. Top right: fluorescence spectrum measured on a 50nm thick film of PMMA doped with TPP. Excitation at 405nm. Bottom right: fluorescence lifetime obtained on the same film. The lifetime of TPP in those films is of the order of 6ns.

concentration of TPP is optimal to avoid self-quenching. Figure 3 presents results from the comprehensive characterization of this dye.

- **Fluorescence enhancement of TPP with the antennas**

When coating TPP films on the nanoantenna samples, we obtained clear evidence of fluorescence enhancement, see Figure 4. On the sample, the antennas are arranged in arrays with a square lattice of constant 4µm. The left hand side image of figure 4 is a confocal fluorescence image of a region of the sample with such antennas, covered by a thin PMMA:TPP film (~30nm thickness). One can see a square array of bright dots in the image: those are due to an enhancement of the fluorescence of the TPP by the presence of an antenna below. The dark spot in the image corresponds to a region of the sample on which the excitation laser has dwelled for a long time during alignment, and has bleached the dye.

The right hand side of figure 4 shows lifetime histograms acquired on a region of the sample without antenna (black curve), and on a region with an antenna (red curve). The black curve can be fitted with a simple exponential (τ=5.5ns), as expected for the unperturbed dye (see Figure 3). The red curve shows two distinct slopes, and can be fitted by a double exponential. This is due to the fact that when observing the emission from the region close to the antenna, photons are collected from unperturbed dyes as well as photons from molecules which fluorescence is enhanced by the presence of the antenna (the detection spot is diffraction limited). The fast decay seen at small delays is τ=2.9

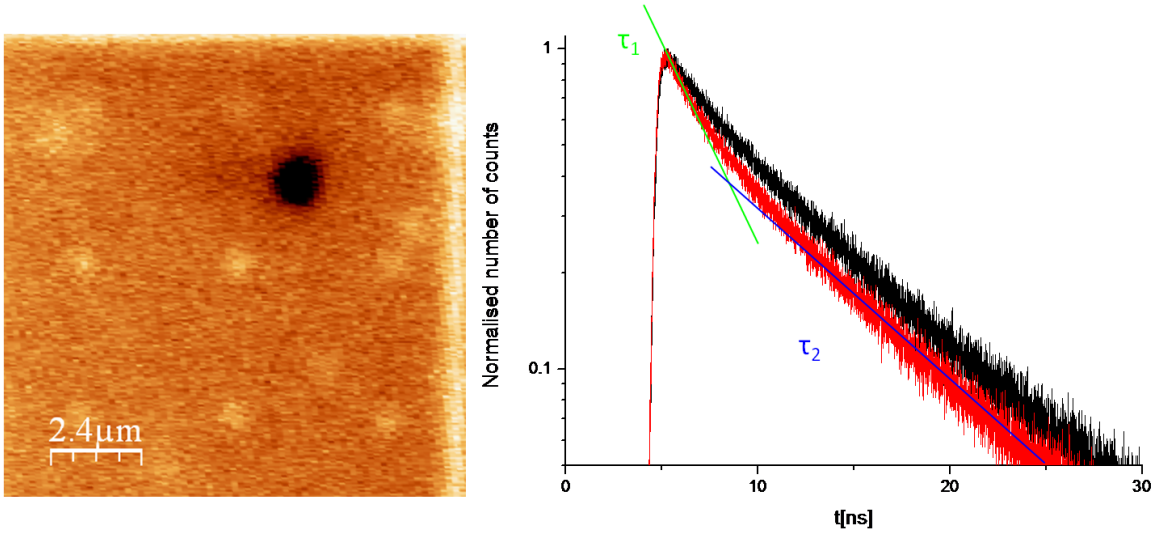

Figure 4: Fluorescence enhancement of TPP by plasmonic antennas. Left: confocal fluorescence image of a region of the sample with antennas. Right: lifetime traces acquired on the background (black) and on an antenna (red).

- **Analytical and numerical framework for STED with strong scatterers**

In parallel, a framework to study STED in situations where highly scattering objects are involved has been developed. This involves the ability to implement excitations with unusual profiles (Laguerre-Gaussian beams, azimuthal polarisations) in Finite Element Method (FEM) simulations, to model the STED depletion beam. FEM or such numerical method is required to model the response of nanoscale scatterers such as the antennas of interest. We are currently preparing these results for publication in a high-profile journal, and will provide a full report in our final deliverable after the end of the project.

Conclusion

Over the last 6 months we identified a new dye more prone to have its fluorescence properties enhanced by nanoantennas. New sets of antennas have been produced, with reproducible properties, and gap small enough to lead to large field enhancements. Combining those two ingredients, we have demonstrated that we can observe fluorescence enhancement fostered by plasmonic antennas. Concurrently, a full modelling of the STED process in the vicinity of nanoantennas has been developed,

which we believe will point towards a new way of biological imaging (details to follow in final report).

We will shortly be able to assess whether STED would allow for a mapping of the lifetime of the dye close to the antennas with a better resolution.

Output thus far

1 journal publication, 2 invited talks.